

## **General Disclaimer**

### **One or more of the Following Statements may affect this Document**

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

**LMSC-HREC TR D568188**

(NASA-CR-150563) THERMAL ENERGY STORAGE  
Final Report (Lockheed Missiles and Space  
Co.) 28 p HC A03/MF A01 CSCL 10C

N78-18520

G3/44 Inclas  
05940

# **THERMAL ENERGY STORAGE**

## **FINAL REPORT**

**Contract NAS8-31100**

**10 February 1978**

**Prepared for**

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
GEORGE C. MARSHALL SPACE FLIGHT CENTER  
MARSHALL SPACE FLIGHT CENTER, AL 35812**

**by**

**P. G. Grodzka**

**E. A. Picklesimer**

**LOCKHEED MISSILES & SPACE COMPANY, INC.  
HUNTSVILLE RESEARCH & ENGINEERING CENTER  
HUNTSVILLE, AL 35807**



## FOREWORD

This report is the final summary of the work accomplished on Contract NAS8-31100, "Thermal Energy Storage Development Study." Ms. B.R. Facemire of the George C. Marshall Space Flight Center was the contract monitor.

The general scope of the study is indicated as follows:

- Survey and review possible concepts for storing thermal energy.
- Evaluate the potentials of the surveyed concepts for practical applications in the low- and high-temperature ranges for thermal control and storage, with particular emphasis on the low-temperature range, and designate the most promising concepts.
- Determine the nature of further studies required to expeditiously convert the most promising concept(s) to practical applications.

The major part of the work has been previously reported (Refs. 1, 2 and 3). Reference 3, a paper that was presented at an AIAA national meeting, is Appendix A of this report.

# CONTENTS

	<u>Page</u>
FOREWORD	ii
INTRODUCTION AND SUMMARY	1
POSSIBLE CONCEPTS FOR CRYOGENIC THERMAL CONTROL	2
RELATED SPACE USE OF ADSORPTION	6
INDICATED DIRECTIONS FOR FURTHER RESEARCH AND DEVELOPMENT	8
REFERENCES	9
Appendix A: AIAA Paper Prepared Under Present Contract	A-i
Appendix B: Thermodynamics of Phase Change, Chemical Reaction and Absorption	B-i

## INTRODUCTION AND SUMMARY

The use of cryogens in space applications appears to be multiplying. Gases for propulsion or atmosphere control purposes are stored as cryogens during flight. Various low-temperature measurements in space also require cryogens for thermal control. Long term storage of cryogens in space will thus become more and more commonplace as space activities multiply. A problem associated with long term storage is that some cryogens must be sacrificed by venting because of heat leaks through the protective super-insulation. Over long periods of time the loss of cryogens by this means could be considerable. One of the objectives of the present program was to investigate some new concepts of thermal control that might lessen the problem of cryogen loss over long periods of time. As indicated in the Foreword, the work accomplished on identification of possible new concepts and on evaluation of their potentials for practical applications has been reported previously. The present report deals only with further consideration of adsorption thermal control, which appears to be the most promising concept for the cryogenic temperature range.

The basis of adsorption thermal control is simple. When a solid phase (adsorbent) adsorbs a gas or vapor (adsorbate), a heat of adsorption is liberated. The heats of adsorption are considerable and usually somewhat larger than heats of evaporation. For example, if 0.128 gram of carbon dioxide is adsorbed on one gram of carbon at 0 C, 19.9 calories are liberated (Ref. 4). Alternatively, when a adsorbate/adsorbent system is heated, adsorbate is liberated and heat is absorbed. Adsorption systems thus behave much like phase change material (PCM) or chemical change systems. Adsorption systems differ from PCM, however, in that adsorption systems are two-component systems and as such possess more flexibility than PCM systems.

A brief review of the thermodynamics of PCM, chemical change, and adsorption systems is given in Appendix B. "The characteristics of the two-component system permit us to choose at will the initial conditions of pressure and temperature independent of one another, thus making it possible for it not only to take the place of a PCM in regions for which no suitable substances exist, but also to replace PCMs in regions where it can offer better pressure conditions" (Ref. 5, note: PCM is substituted in the preceding quote for the original C-stage notation). In the low-temperature region suitable PCM materials are in short supply. In fact, the lowest melting potential PCM thus far identified in the present study has a melting temperature of 129 K (Ref. 3). For storage of liquid oxygen, hydrogen, and helium, the required temperatures are in the range of about 90 to about 1.5 K.

In the following section a number of concepts are presented and their operation discussed. A subsequent section presents indicated directions for further research and development.

From the consideration presented in the following sections, it is concluded that adsorption thermal control appears as a very promising concept in the cryogenic temperature region. More detailed analyses and tests of particular applications, however, are required for a realistic estimate of its potential.

#### POSSIBLE CONCEPTS FOR CRYOGENIC THERMAL CONTROL

A number of preliminary concepts utilizing adsorption thermal control were presented in a previous paper that was written under the present contract (Ref. 3). One of the concepts presented in that paper, as well as some further arrangements that have suggested themselves since, are shown in Fig. 1.

In Case (a) cryogen vented from a storage tank would be collected on charcoal or other suitable adsorbent. Just before a measurement is to be made, the whole apparatus would be cooled in space to about 100 K or, by

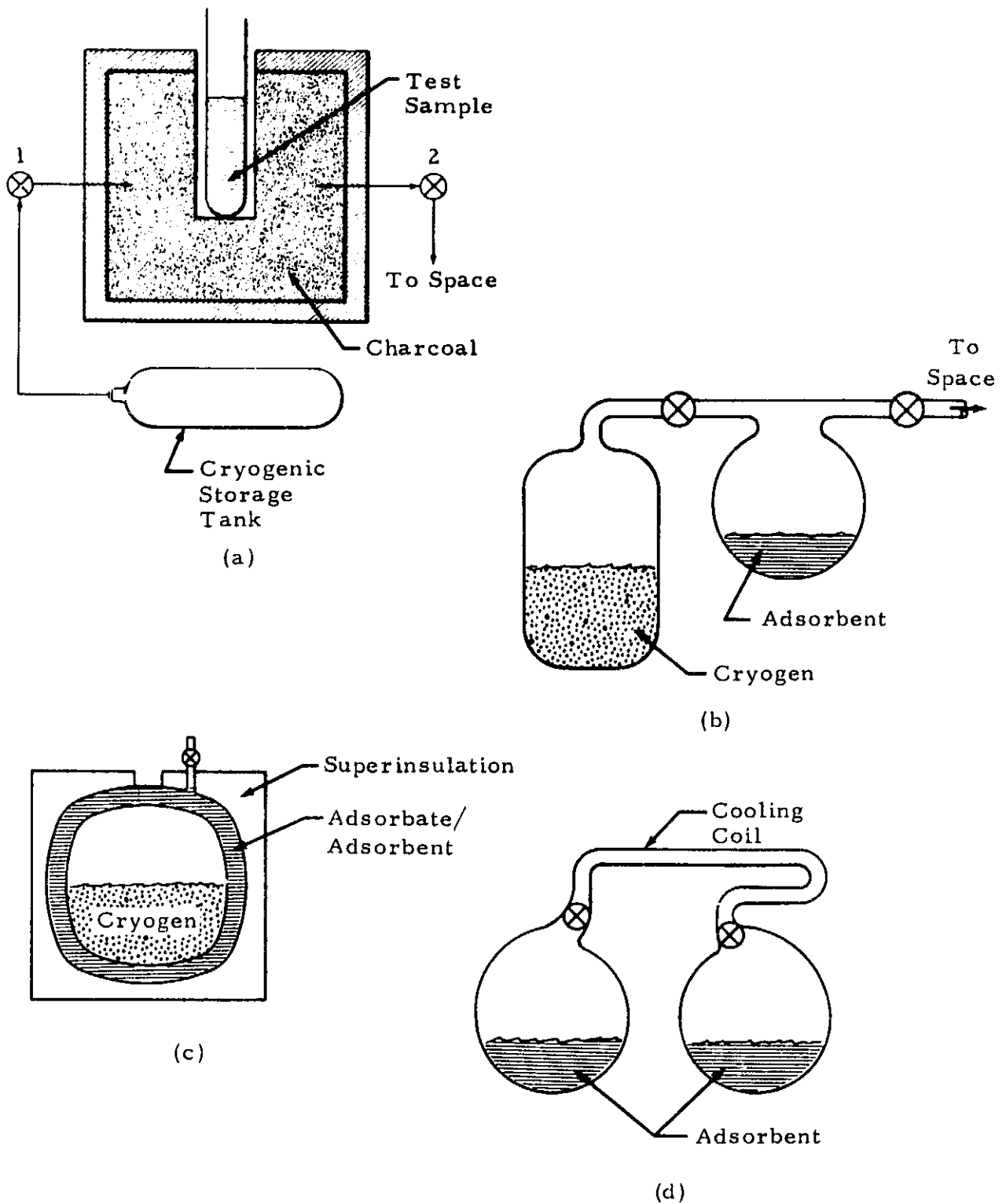


Fig. 1 - Concepts for Cryogenic Thermal Control

some other means, to even lower temperatures. Further reduction in temperature would then be achieved by venting adsorbed gas to space. The arrangement in Case (a) is very similar to desorption cryostats used previously to attain very low temperatures. For example, by desorbing helium from charcoal it was possible to hold a temperature of 21 K for over 30 minutes when 100 mW were being generated in the calorimeter in addition to the normal heat leaks (Ref. 6). In another study, temperatures in the range of 4 to 14 K were maintained with a constancy of  $\pm 0.001$  K by helium desorption from charcoal (Ref. 7).

In Case (b) cryogen that would otherwise be vented to space would be collected on absorbent. The heat of adsorption can either be radiated or vented into space. Further venting of the adsorbed cryogen vapor would have the effect of cooling the remaining gas, adsorbent, and container to liquefaction. Thus, a portion of the normal boil-off could be saved. Figure 2 presents a more sophisticated scheme for recovering part of the normal cryogenic boil-off. The systems operates as follows:

Step No.

- 1 Chambers A and B are initially evacuated. Chamber B contains activated charcoal.
- 2 Valves 1 and 2 open, filling chambers A and B. Heat is given off by the charcoal and chambers A and B are allowed to reach thermal equilibrium.
- 3 Valve 3 is open slowly, venting chamber A to space and then closed.
- 4 Valve 2 is opened, filling chamber A.
- 5 Valve 4 is opened slowly, venting chamber B and then closed. The charcoal absorbs heat from the condensing gas in chamber A. When thermal equilibrium is reached, valves 2 and 4 are closed.
- 6 Valves 1 and 5 are opened. Heat liberated by charcoal causes the pressure to rise in chamber A driving the liquid cryogen back into the tank. After equilibrium is reached, valves 1 and 5 are closed. Then, go to step 3.



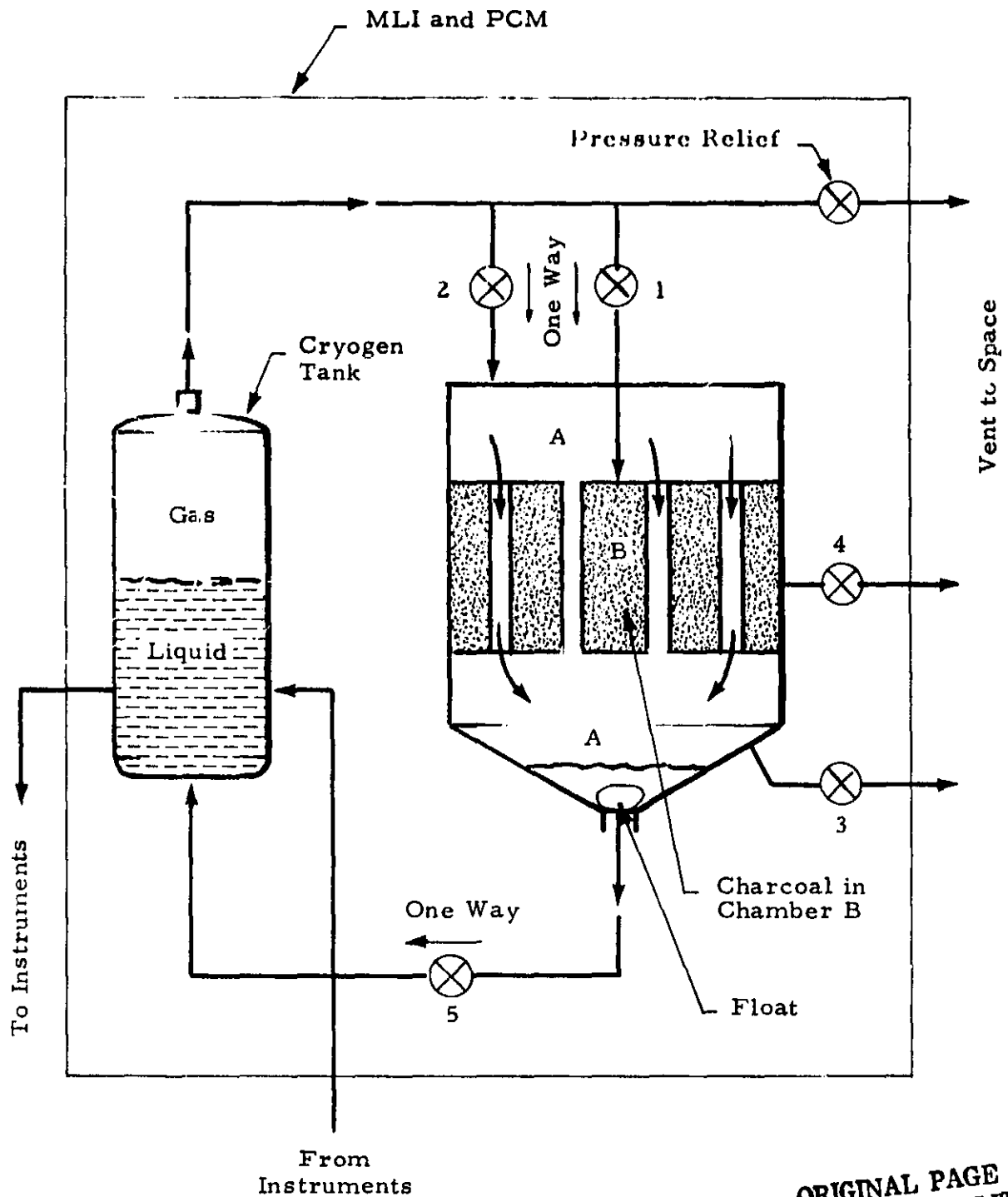


Fig. 2 - Adsorption Recovery System

A simple process analysis using the latent heat of helium, the heat of adsorption of helium on charcoal and assuming a 70% heat transfer efficiency was performed. The results indicate that it may be possible to recover as much as 50% of the boiloff from cryogen systems.

Desorption has been reported previously as a means to produce low temperature either directly (Ref. 5) or as a precooling technique (Ref. 8).

In Case (c) temperature control is maintained around the cryogen by venting to space. The advantage of this arrangement over direct venting to space lies in more precise temperature control and in the very large heat capacity of saturated charcoal (Ref. 6).

Case (d) represents a refrigerator. Thermal energy desorbs adsorbate from adsorbent in one bulb. As a result of the desorption, the pressure builds. The gas under pressure is then expanded through a pressure relief valve, the expansion causing a cooling in the cooling coil. Expanded gas is collected on adsorbent in the other bulb which is maintained at a lower temperature than the heated bulb. When adsorbate is all expelled from the first bulb, the process can be repeated in reverse. An adsorption refrigerator was developed and used in the late 20s and early 1930s (Refs. 9 and 10). Why it faded from use is a mystery. Apparently the device was quite efficient. For space application, an adsorption refrigeration unit appears attractive.

## RELATED SPACE USE OF ADSORPTION

Adsorption on molecular sieves was suggested as a means by which oxygen from a stored solid state could be delivered in a breathable state (Ref. 11). The experimental test arrangement for the concept is shown in Fig. 3.

The working vessel consists of a double-wall container, evacuation lines, a pressure sensing tube, and an evacuation line leading into the space between the double walls. The space between the double walls can be evacuated to provide an insulation space or filled with helium gas to serve as a

ORIGINAL PAGE IS  
OF POOR QUALITY

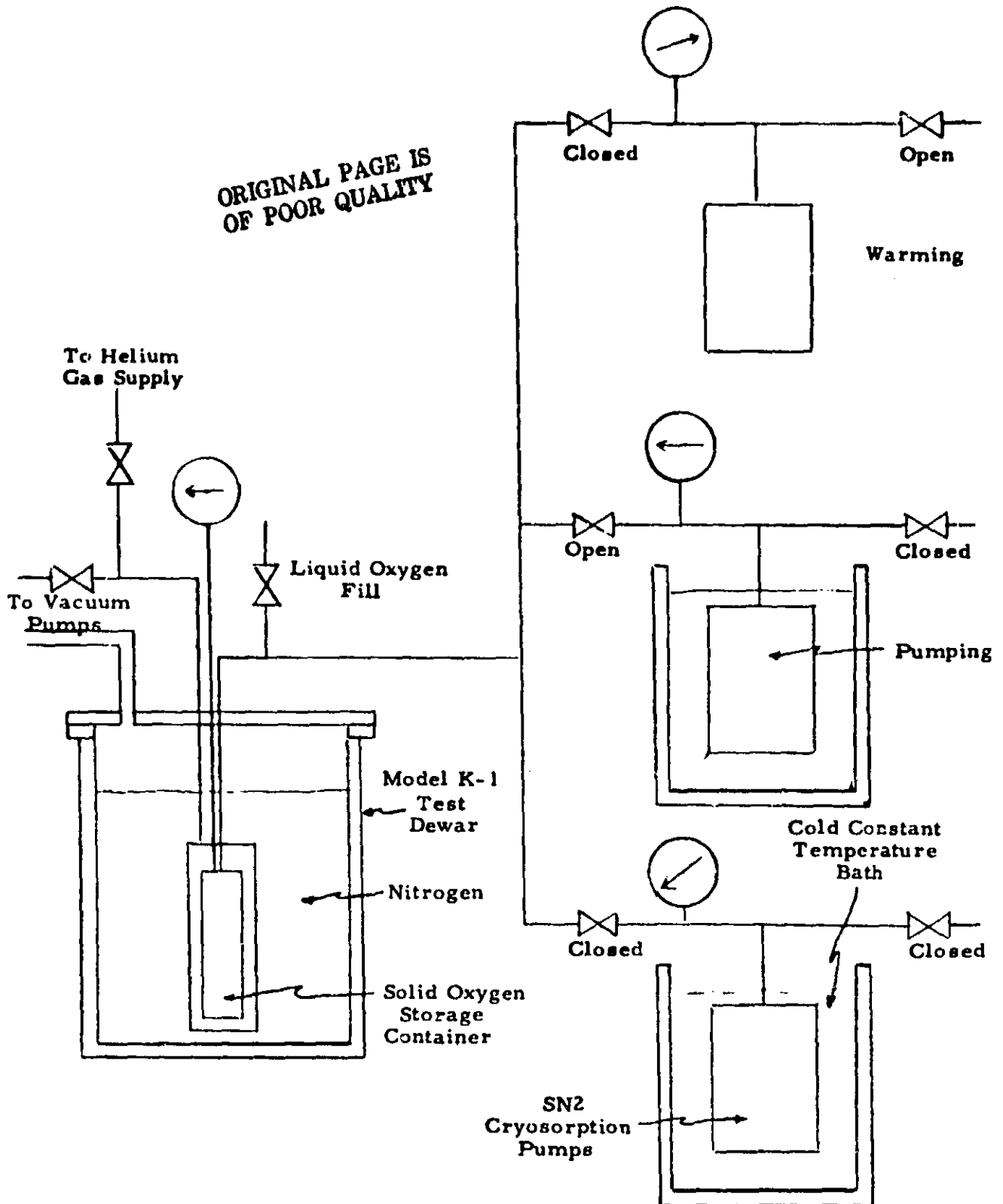


Fig.3 - Experimental Setup-Transport by Adsorbents (Ref. 11)

thermal conductor. The pressure sensing tube from the oxygen container was connected to a pressure gauge to indicate the state of the oxygen.

The cryosorption pump provides a low pressure over the stored oxygen and acts as a collector and pressure raising device for the subliming oxygen. Valves are provided so that the pumps can be alternately and sequentially removed from the low-temperature bath for measurement of the amount of oxygen evolved at a breathable pressure. By using three cryosorption pumps, this can be done on a continuous basis.

The gaseous oxygen desorbed from the cryosorption pumps by heating was condensed and measured. Condensing was accomplished by surrounding the oxygen collection tube with liquid nitrogen. The amount transferred was determined by measuring the level of the liquified oxygen with a cathetometer.

#### INDICATED DIRECTIONS FOR FURTHER RESEARCH AND DEVELOPMENT

Detailed analyses of the suggested concepts are required before rigorous statements of possible advantages can be made. Also more information is needed on the physical properties of adsorbate/adsorbent systems and their behaviors under heating and cooling conditions, i.e.; Are adsorption and desorption reversible? What is the effect of long term thermal cycling? What are the heat capacities of various adsorbate/adsorbent systems? Systems in which chemical reactions occur, i.e., hydride formation, ammoniate formation, etc., should also be examined as possible candidate for thermal control applications. Finally, an experimental test of the most promising concept should be performed.

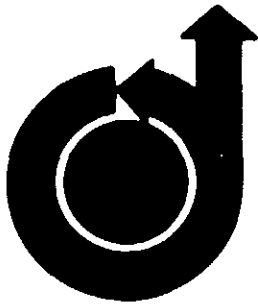
## REFERENCES

1. Grodzka, P.G., "Thermal Energy Storage: Interim Report," LMSC-HREC TR D496600, Lockheed Missiles & Space Company, Huntsville, Ala., November 1975 (Contract NAS8-31100).
2. Grodzka, P.G., and L. E. Connor, "Thermal Energy Storage: Second Interim Report," LMSC-HREC TR D497048, Lockheed Missiles & Space Company, Huntsville, Ala., 29 October 1976 (Contract NAS8-31100).
3. Grodzka, P.G., E. A. Picklesimer and L. E. Connor, "Cryogenic Temperature Control by Means of Energy Storage Materials," Paper 77-763, AIAA 12th Thermophysics Conference, Albuquerque, 27-29 June, 1977 (Appendix A to this report).
4. Gregg, S. J., The Surface Chemistry of Solids, Second Edition, Reinhold, New York, 1961, p.35.
5. Simon, F., "On the Desorption Method," Physica, Vol. IV, No. 10, October 1937, pp. 879-899.
6. Rose-Innes, A. C., and R. F. Broom, "A Simple Desorption System for Obtaining Temperatures Above That of Liquid Helium," J. Sci. Instr., Vol. 33, 1956, p. 31.
7. Jackson, L. C., and H. Preston-Thomas, "A Small Gas-Cooled Cryostat for Temperatures Between 4K and 14K," J. Sci. Instr., Vol. 28, 1951, pp. 99-101.
8. Keyes, F. G., H. T. Gerry, and J. F. G. Hicks, Jr., "The Production of Liquid Hydrogen Without Expensive Equipment. Low Temperature Studies No. I," J. Am. Chem. Soc., Vol. 59, 1937, pp. 1426-1437.
9. Miller, E. B., "The Development of Silica Gel Refrigeration," Refrigerating Engineering, Vol. 17, 1929, pp. 103-108.
10. Hulse, G. E., "Freight Car Refrigeration by an Adsorption System Employing Silica Gel," Refrigerating Engineering, Vol. 17, 1929, pp. 41-54.
11. Ohern, J. E., and T. W. Lawson, Jr., "Cryogenic Solid Oxygen Storage and Sublimation Investigation," AMRL-TR-68-105, Wright Patterson Air Force Base, Dayton, Ohio, December 1968.

12. Walton, H. F., Inorganic Preparations, Prentice-Hall, New York, 1948, p. 22.
13. Dushman, S., Scientific Foundations of Vacuum Technique, Second Edition, J. M. Lofferty, Editor, Wiley, New York, 1962.

Appendix A  
AIAA PAPER PREPARED  
UNDER PRESENT CONTRACT

Note: In the concept presented in Fig. 5 in the AIAA paper, some variation in temperature and pressure occurs as the result of energy absorption or liberation.



ORIGINAL PAGE IS  
OF POOR QUALITY

**77-763**

**Cyrogenic Temperature Control by Means of  
Energy Storage Materials**

P.G. Grodzka, E. Picklesimer, and L.E.  
Connor, *Lockheed Missiles & Space  
Company, Huntsville, Ala.*

**AIAA 12th THERMOPHYSICS  
CONFERENCE**

Albuquerque, N. Mex./June 27-29, 1977

For permission to copy or republish, contact the American Institute of Aeronautics and Astronautics,  
1290 Avenue of the Americas, New York, N.Y. 10019.



# CRYOGENIC TEMPERATURE CONTROL BY MEANS OF ENERGY STORAGE MATERIALS\*

P. G. Grodzka\*\*, E. A. Picklesimer† and L. E. Connor††

Lockheed Missiles & Space Company, Inc.  
P. O. Box 1103, Huntsville, Alabama 35807

## Abstract

Long term storage of cryogenics in space is important for fuel conservation and for efficient operation of astronomical instruments. Although multiple layer insulation (MLI) has been used exclusively for insulating cryogenic storage tanks, improvement in thermal control is indicated by use of energy storage materials (ESM) in conjunction with MLI. ESMs store large amounts of thermal energy by means of sensible heat, heat of fusion, or reaction heat. This paper presents recent results of concept evaluation and experimental studies on phase change and gas adsorber ESMs. A differential thermal analysis (DTA) technique was utilized in the experimental studies. Gas adsorber ESMs appear to offer unique possibilities for cryogenic thermal control.

## I. Introduction

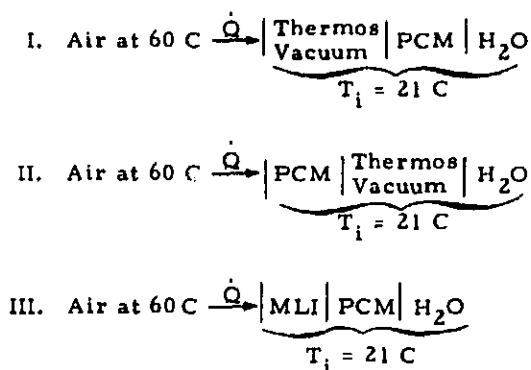
The problem of storing cryogenics during long-term space voyages has been approached in the past primarily from the viewpoint of multiple layer insulation (MLI) improvement. The concept of thermal control by means of physical or chemical reaction heats has not yet been explored for cryogenic temperature regions (250 K or less). Physical or chemical changes offer the advantages of being able to accommodate heating-cooling cycles without significant changes of temperature. The objectives of the present study, therefore, were to conduct such an exploration and to perform some preliminary experimental tests of energy storage material (ESM) effectiveness.

The nomenclature ESM used in this paper refers to materials that store and liberate large amounts of thermal energy by means of mechanisms such as sensible heat, heat of fusion, and physical or chemical reaction heat. Because of the ability to store and liberate large amounts of thermal energy, ESMs are capable of acting as thermal control devices. In previous works (Refs. 1 through 3), the theoretical basis of the ESM concept was considered at some length. Thermal energy storage by sensible heat, chemical potential energy, and latent heat of fusion were included. In the present study, some results of concept evaluations and laboratory ESM tests are presented. A DTA (differential thermal analysis) approach was utilized in the laboratory tests. Experimental and analytical results from the effort reported herein indicate that ESMs can offer added advantages in existing thermal control concepts.

## II. Evaluation of Cryogenic ESM Thermal Control Concepts

Two possible ESM-MLI arrangements suggest themselves. These are shown in Figure 1. In concept A of Figure 1, the ESM would have a transition temperature near the desired storage temperature of the cryogen. In concept B, the ESM would be on the outside of the superinsulation.

In order to obtain an idea of how such systems might actually operate, simplified models were developed for input into Lockheed's Thermal Analyzer Computer Program. This program solves those differential equations that represent the time dependent heat conduction problem (Ref. 4). The following three models were compiled and run.



where  $T_i$  = initial temperature

The PCM utilized in these evaluations was lithium nitrate trihydrate. Lithium nitrate trihydrate changes from a solid to a liquid at approximately 29 C with a heat of fusion of 331 kJ/kg (79 cal/gm, 142 Btu/lbm). The thermal properties utilized in the calculations are given in Table 1. The heat of fusion of the PCM was simulated by modeling a large step change in its heat capacitance for the solid state at the melt temperature. This step change correctly simulated the absorption of the necessary heat for the PCM to change phase or melt. After complete melting occurred, the heat capacitance then involved a large step change to that representing the PCM in the liquid state.

Figure 2 shows the temperature time histories of the nodes for the models as indicated. Node 1 in all cases represents an infinite amount of air at a constant temperature of 60 C. At time zero, nodes 2, 3 and 4 are at 21 C. For Case I, it is obvious that the flattening of the temperature time histories for nodes 2, 3 and 4 are significant. This

\*Work performed for NASA-Marshall Space Flight Center under Contract NAS8-31100.

\*\*Staff Scientist, Member AIAA; †Research Specialist; ††Research Engineer, Sr.

flattening represents the energy being stored in the PCM as the heat of fusion. For case II, there is no significant flattening and a fairly steep rate of temperature change is observed in all three nodes.

For Case III, the temperature of nodes 3 and 4 do not change for the length of time that was run. It is obvious from observing the three cases that multilayer insulation, in a simple model such as run here, is by far the best insulator.

The results of the three cases indicate that concept A of Figure 1 in which MLI is employed offers by far the best arrangement for thermal control of cryogen, i.e., water in the simple model. The results, furthermore indicate that in cases where MLI is unfeasible an ESM by itself as insulation offers a definite advantage (concept A with vacuum). MLI it may be mentioned is vulnerable to compression, outgassing, and tearing.

### III. Experimental Determination of PCM Characteristics

Several low temperature phase change materials (PCM) were recommended for further study by Grodzka and others in previous studies (Refs. 2 and 5). Table 2 lists materials which are prime candidates requiring further investigation and materials (candidates) which appear interesting but require further data. The prime candidates in Table 2 have heats of fusion greater than 167 kJ/kg (40 cal/gm) and freezing points less than 0 C.

#### Low Temperature Differential Thermal Analysis (DTA) Apparatus

A simplified DTA apparatus was set up to evaluate the low temperature PCM candidates listed in Table 1. Grodzka and Connor (Ref. 3) described how the DTA can be used to screen and test potential ESM candidates. Figure 3 shows the essential components of the DTA apparatus used for the tests described in this paper. The test consisted of weighing a fixed volume of PCM in a crucible. Liquid nitrogen (LN) was placed in the dewar and the crucible was lowered into the dewar. The distance between the crucible and the surface of the LN determined the cooling rate and the temperature of the PCM. Temperatures as low as -160 C were obtained without actually submerging the PCM in the LN. The temperature difference between the PCM candidate and the reference material was recorded on a four-channel millivolt recorder. In addition, the temperature of the PCM was recorded using an electronic reference junction. All temperature measurements were made with copper-constantan thermocouples. Figure 4 shows the type of trace obtained. From the area under the  $\Delta T$  spike, the latent heat of phase change can be determined from the equation

$$L = \frac{CA}{m} \quad (1)$$

where  $m$  = mass,  $L$  = latent heat of fusion,  $A$  = the area under the  $\Delta T$  freezing curve, and  $C$  = a constant. The constant  $C$  can be evaluated from a freezing curve of a material, whose latent heat is known, water for example.

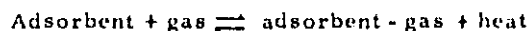
Table 3 summarizes the results of DTA tests run on some of the PCM candidates listed in Table 2. The data in Table 3 indicate that heptanone-4

and N-dodecane would behave well as PCMs. The freezing point of these two materials is relatively high, however. The lower melting materials with high latent heats exhibited nucleation problems. Such a situation is not surprising, as previously discussed (Ref. 1). More work on identifying suitable nucleation catalysts is indicated.

Carbon disulfide freezes well and has a low freezing temperature, but, unfortunately has a relatively low heat of fusion.

### IV. Adsorption ESMs

The adsorption process can be represented as



Heats of adsorption are fairly substantial. For example, the heat of adsorption of one mole of carbon dioxide on charcoal is on the order of 773 kJ/kg (185 cal/gm) (Ref. 6). One possible concept for utilizing adsorption heats for thermal control of stored cryogens is shown in Figure 5. When adsorbed cryogen vapor is released because of a heat leak through the insulation (exterior heat source), it would naturally migrate toward the coldest part of the apparatus. This would be the liquid cryogen itself. There the vapor would condense. When heat is lost through the superinsulation to the surrounding environment, some cryogen would evaporate and migrate back into the charcoal area where it would be adsorbed.

Figure 6 shows a simple concept for controlling the temperature of a test sample in a space laboratory. Assume that it is desired to maintain the temperature of a test sample at -50 C. If the sample cools off slightly, valve 1 may be opened exposing the charcoal to additional gas. Adsorption of the gas on the charcoal liberates heat to balance the heat loss of the sample. On the other hand, if the sample heats up, valve 2 is opened degassing the charcoal and absorbing heat from the sample. In a prior study (Ref. 7), an apparatus somewhat similar to that shown in Figure 6 and utilizing helium was able to maintain a temperature of 21 K when 100 mW was generated in addition to the normal heat leak. A small helium desorption cryostat was able to maintain a temperature constancy of  $\pm 0.001$  K for periods of up to one and one-half hours by manual control (Ref. 8). In still another study (Ref. 9), desorption of hydrogen from charcoal was utilized to produce temperatures of about -253 C.

The actual heat realized in any practical space system depends on a number of variables. These include temperature and pressure at which the adsorption is taking place as well as the extent of adsorption already existing. Other concerns of practical importance are those of reversibility and of adsorption/desorption kinetics. In order to obtain an idea of the problems that might be associated with adsorption ESM thermal control a simple evaluation apparatus was devised (Figure 7).

The charcoal was initially degassed for 24 hours by closing valves 1 and 2 and opening valve 3 and heating to 250 F. Valve 3 was closed and the container of charcoal was placed in a bath of liquid nitrogen (LN) as shown in Figure 7. Valve 1 was then opened and the container of charcoal

was pressurized to 1 atm with dry nitrogen gas. When equilibrium was reached, valve 1 was closed. At this point valve 3 was opened, degassing the charcoal, and the temperature difference between the bath and the charcoal was recorded until equilibrium was again attained. Then valve 3 was closed and valve 1 was opened pressurizing the container of charcoal while recording the temperature difference ( $\Delta T$ ). The latter procedure was repeated four or more times to show reproducibility. Figure 8 shows a typical  $\Delta T$  trace during the degassing and the adsorption process. It may be noted that the degassing processes cooled the charcoal significantly below the temperature of the LN bath. The maximum difference in the areas under the degassing and adsorption curves was less than 8% throughout consecutive cycles indicating that the cyclic adsorption process at constant temperature is more than 90% reversible.

A combination of the preceding two concepts has also been suggested for reducing the amount of cryogen boil-off. In this concept, part of the boil-off would be adsorbed on absorbent. Subsequent release of the adsorbed cryogen would lower the temperature sufficiently to liquify another portion of the boil-off. Further studies of concept advantage, however, are needed.

### Conclusions

The results of present exploratory studies indicate that:

- An ESM shield surrounded by MLI offer the best protection for a cryogen store. In cases where MLI cannot be used, furthermore, an ESM by itself would still offer a definite advantage.
- Experimental tests indicate that heptanone-4 and N-dodecane behave well as PCMs at temperatures of -33 C and -10 C. Lower melting candidates show nucleation problems. A search for suitable nucleation catalysts for these materials is indicated.
- Experimental studies of gas adsorption ESMs indicate that such materials are very promising for cryogenic temperature control.

### References

1. Grodzka, P. G., "Thermal Control of Spacecraft by Use of Solid-Liquid Phase-Change Materials," AIAA Paper No. 70-12, AIAA 8th Aerospace Sciences Meeting, New York, 19-21 January 1970.
2. Grodzka, P. G., "Thermal Energy Storage, Interim Report," LMSC-HREC TR D496600, (Contract NAS8-31100), Lockheed Missiles & Space Company, Huntsville, Ala., November 1975.
3. Grodzka, P. G., and L. E. Connor, "Thermal Energy Storage, Second Interim Report," LMSC-HREC TR D497048, (Contract NAS8-31100), Lockheed Missiles & Space Company, Huntsville, Ala., October 1976.
4. Pond, J. E., "A Small Thermal Analyzer Package with Simplified Input," LMSC-HREC D162533, Lockheed Missiles & Space Company, Huntsville, Ala., February 1971.
5. Pizzolato, P. J., and R. A. Farmer, "Phase Change Thermal Control Development; Technical Summary Report," MCR-73-11, Martin Marietta Corp., Denver, February 1973.
6. Durhman, S., Scientific Foundation of Vacuum Technique, 2nd Edition, J. M. Lafferty, Editor, John Wiley, New York, 1962, p. 406.
7. Rose-Innes, A. C., and R. F. Broom, "A Simple Desorption System for Obtaining Temperatures Above that of Liquid Helium," J. Sci. Instr., Vol. 33, 1956, p. 31.
8. Jackson, L. C., and H. Preston-Thomas, "A Small Gas-Cooled Cryostat for Temperatures Between 4 K and 14 K," J. Sci. Instr., Vol. 28, 1951, pp. 99-101.
9. Andrews, D. H., R. K. Witt, and E. Crigler, "The Production of Low Temperatures by Desorption of Gases from Charcoal," Refrigeration Engineering, Vol. 19, 1930, pp. 177-180.

Table 1 Properties of materials

	$\rho$ (kg/m <sup>3</sup> )	$C_p$ (J/kg-K)	K (J/sec-m-K)	Material Thickness (m)
PCM (LiNO <sub>3</sub> · 3 H <sub>2</sub> O)		T < 300 K 2041 T > 300 K 4190	0.630	0.0127
Thermos Vacuum	2723	718	0.0144	0.00508
MLI	144	1257	0.0007	0.00508
H <sub>2</sub> O	1000	4190	0.630	0.00508

Table 2 Low temperature PCM candidates

Prime Candidates	Melting Point (K)	Heat of Fusion kJ/kg (cal/gm)
Dodecane <sup>*</sup>	263	215 (51.4)
Heptanone-4 <sup>*</sup>	240	>209 (>50)
Tricaproin <sup>*</sup>	213	>209 (>50)
Ammonia <sup>*</sup>	195	333 (80)
2NH <sub>3</sub> • H <sub>2</sub> O	194	188 (45)
NH <sub>3</sub> • H <sub>2</sub> O	194	171 (41)
NH <sub>3</sub> • 2H <sub>2</sub> O	176	130 (31)

Candidates	Melting Point (°C)	Boiling Point (°C)
H <sub>2</sub> SO <sub>4</sub> • H <sub>2</sub> O	-39.51	
Acetone Hydrate	-35	
B <sub>2</sub> H <sub>5</sub> Br	-104	~10
Si <sub>3</sub> H <sub>8</sub>	-117.4	52.9
Si <sub>4</sub> H <sub>10</sub>	-93.5	80
COS	-138	-48
(SiH <sub>3</sub> ) <sub>2</sub> O	-144	-15.2
(SiH <sub>3</sub> ) <sub>3</sub> N	-105.6	52
CS <sub>2</sub>	-108.6	46.3

<sup>\*</sup> Candidates recommended in prior study (Ref. 5).

Table 3 Test summary of PCM evaluations

Material	Reference	Freezing Point (°C)		Latent Heat kJ/kg (cal/gm)		Freezing Pt. Depression (°C)
		Reported	Test Results	Reported	Test Results	
Carbon Disulfide	H <sub>2</sub> O	-108.6	-113.6	54.4 (13.0)	48 (11.7)	10.4
NH <sub>3</sub> - H <sub>2</sub> O Eutectic	Ethyl Alcohol	-79	NFO <sup>*</sup>	171 (41)		
Tricaproin		-60	NFO <sup>**</sup>	>209 (>50)		
Heptanone-4	H <sub>2</sub> O	-33.0	-32.0	>209 (>50)	226 (54.0)	3.0
N-Dodecane	H <sub>2</sub> O	-10.0	-9.2	>209 (>50)	293 (70.1)	1.3

<sup>\*</sup> NFO - no freezing obtained.

<sup>\*\*</sup> A variety of freezing catalysts were tried without success.

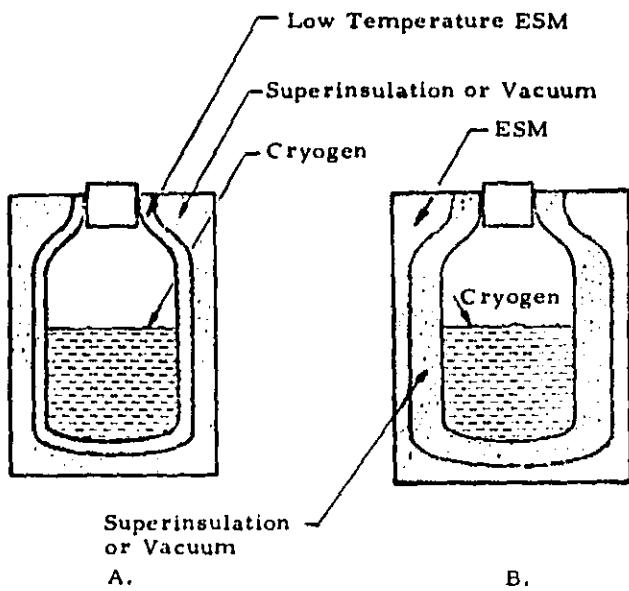


Figure 1. Possible concepts for cryogenic thermal control.

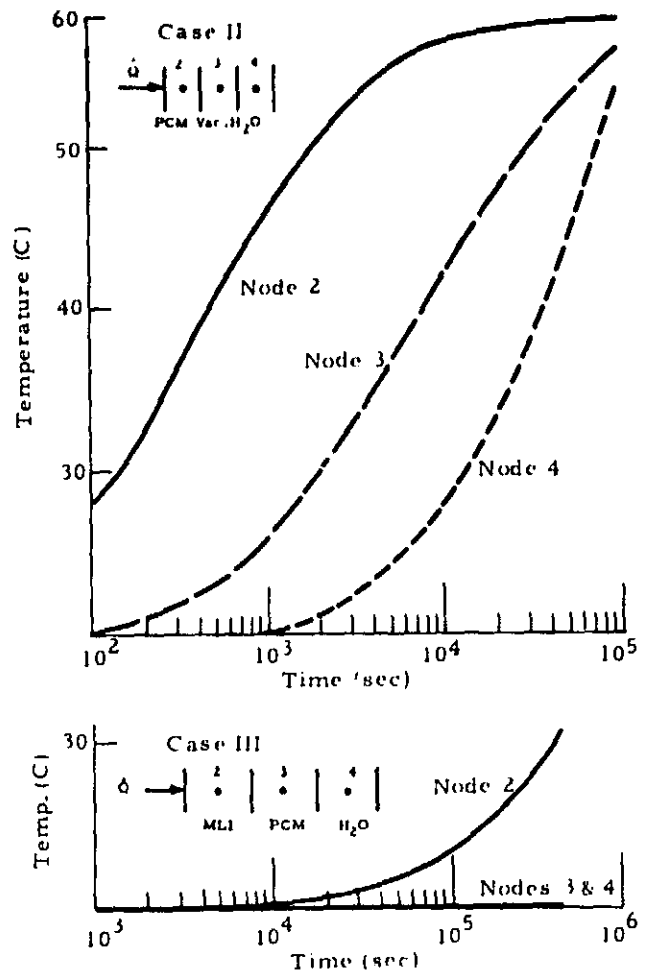


Figure 2. Continued

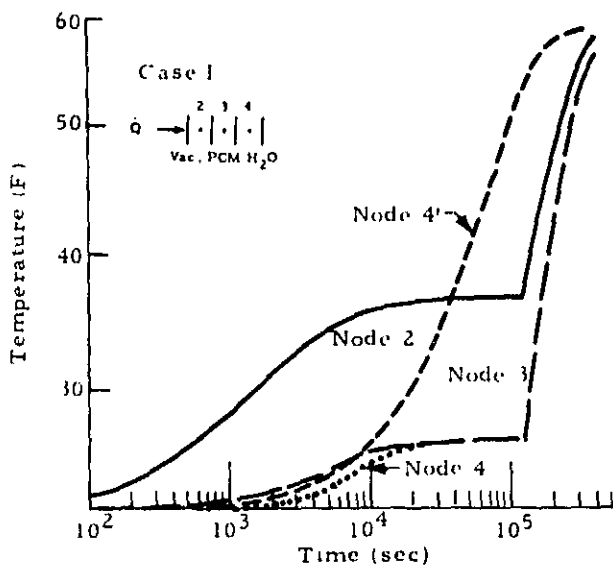


Figure 2. Temperature-time histories for nodes 2, 3 and 4 for cases I, II and III. (Node 4' represents water if no PCM were used, i.e., move node 4 into the node 3 position.)

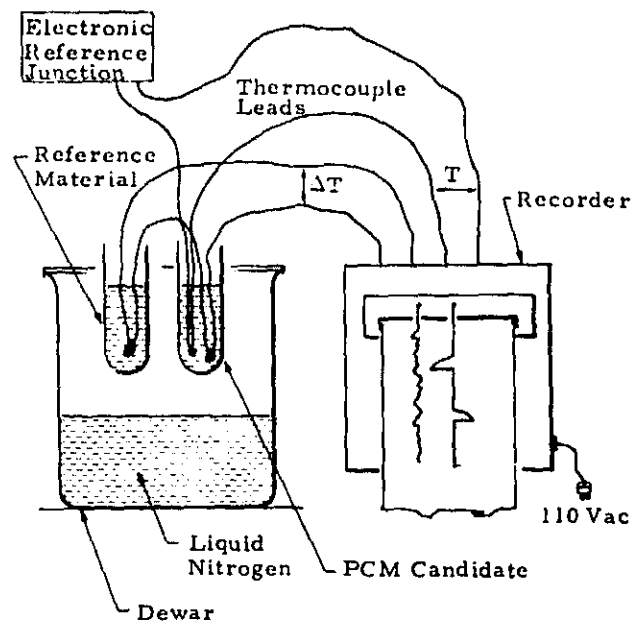


Figure 3. Simplified DTA model apparatus.

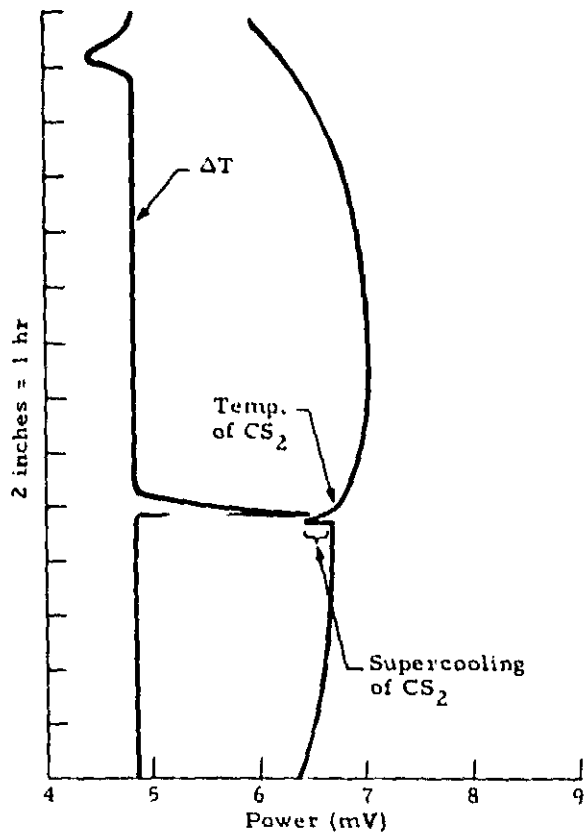


Figure 4. T and  $\Delta T$  curve for  $\text{CS}_2$

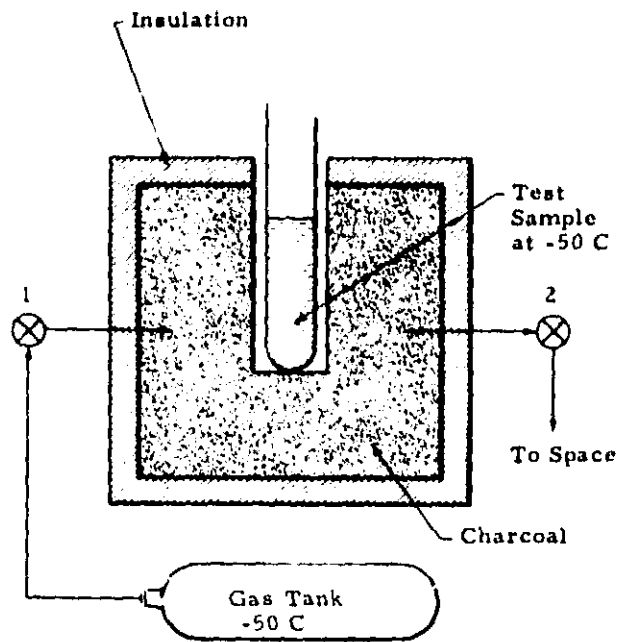


Figure 6. Temperature control concept using gas adsorption on charcoal.

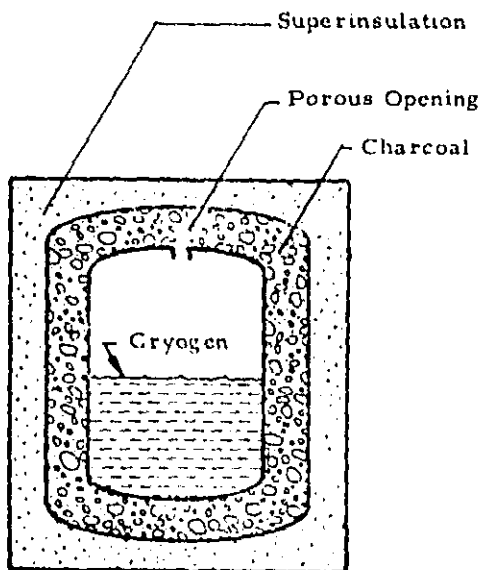


Figure 5. Cryogen thermal control concept utilizing an adsorption ESM.

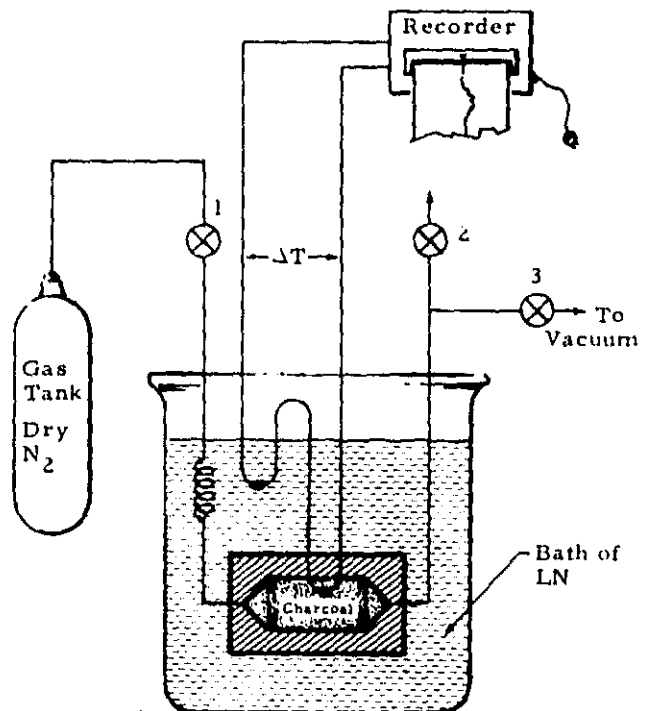


Figure 7. Experimental apparatus for absorption ESM evaluation.

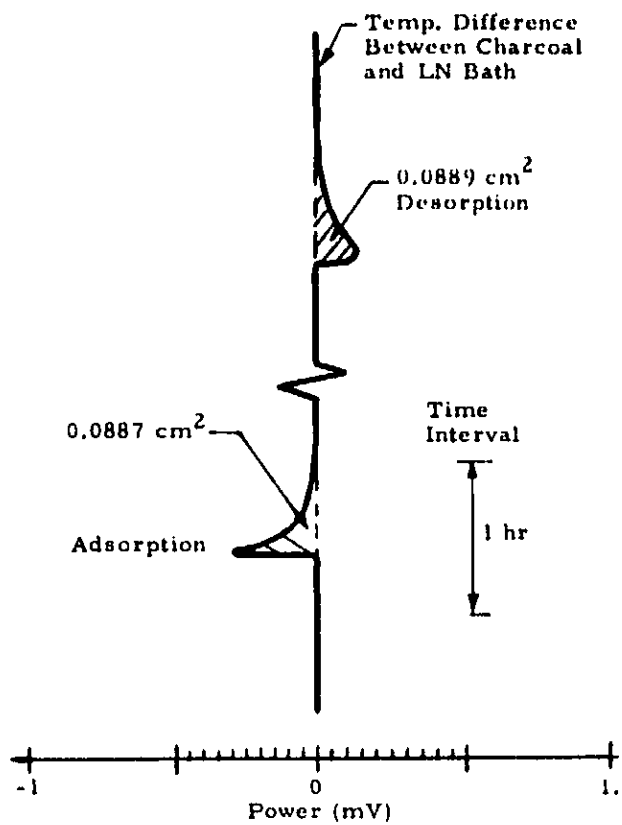


Figure 8. Adsorption on charcoal.

ORIGINAL PAGE IS  
OF POOR QUALITY

Appendix B  
THERMODYNAMICS OF PHASE CHANGE,  
CHEMICAL REACTION AND ABSORPTION



# Appendix B

Consider a container of PCM (water) to which heat can be added or subtracted and also the corresponding phase diagram, i.e., Figs. B-1a and B-1b.

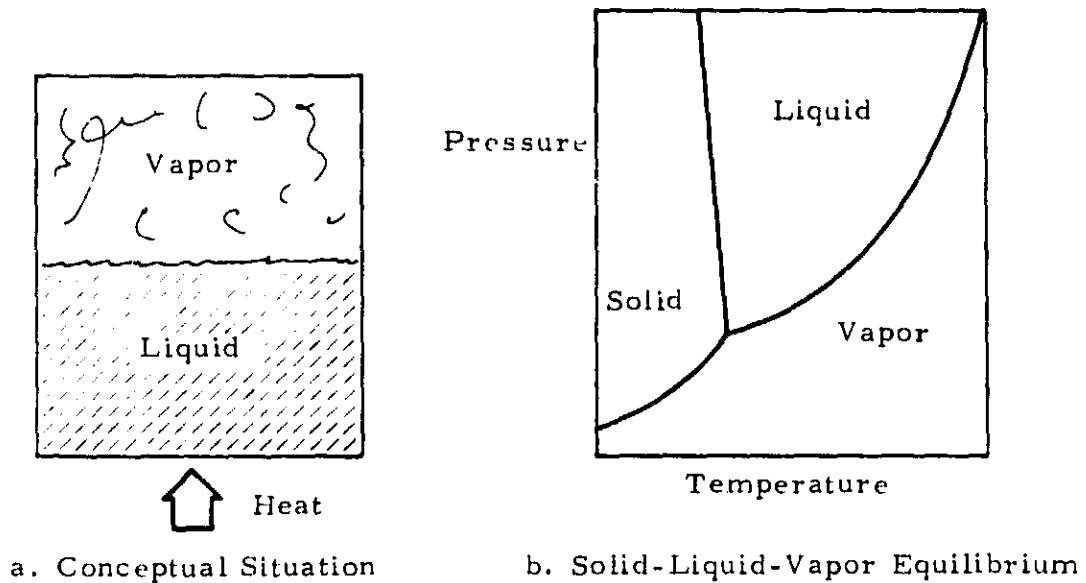


Fig. B-1 - Schematics for Consideration of Practical Thermodynamics of Liquid-Vapor Phase Change

ORIGINAL PAGE IS  
OF POOR QUALITY

If the container is entirely sealed so that no material can enter or leave, heat addition will raise both the temperature and pressure, as along line OA if it is assumed that the vaporization process is extremely rapid compared to the rate of heat transfer. If the container is provided with a piston arrangement, however, so that heat addition can occur at essentially constant pressure, our system achieves zero degrees of freedom. Thus heat can be added or subtracted without the temperature changing. This result can be deduced from the well-known phase rule

$$f = C - P + R$$

where

$f$  = the number of intensive variables that can be changed without changing the number of phases

$C$  = the number of independently variable components

$P$  = the number of phases

$R$  = the total number of unconstrained intensive variables.

The term  $f$  can also be viewed, for purposes of the present report, as the number of intensive variables that can be changed by heat addition. The case where  $f = 0$  is, of course, very advantageous for thermal control applications. Zero freedom degree systems can transfer heat at essentially constant temperature and pressure.

A chemical reaction can behave like a phase change reaction, i.e.,



$$F = C - P + 2 = 2 - 3 + 2 = 1$$

or

$$F = 0 \text{ if pressure is constrained.}$$

Figure B-2 shows the phase diagram for the  $\text{CuSO}_4$  system. Thus as long as three phases are present and the pressure is constrained to a constant value, heat can be added at constant temperature. It is an interesting note that if temperature is constrained to a constant value, water vapor can be added to or subtracted from the system at constant pressures.

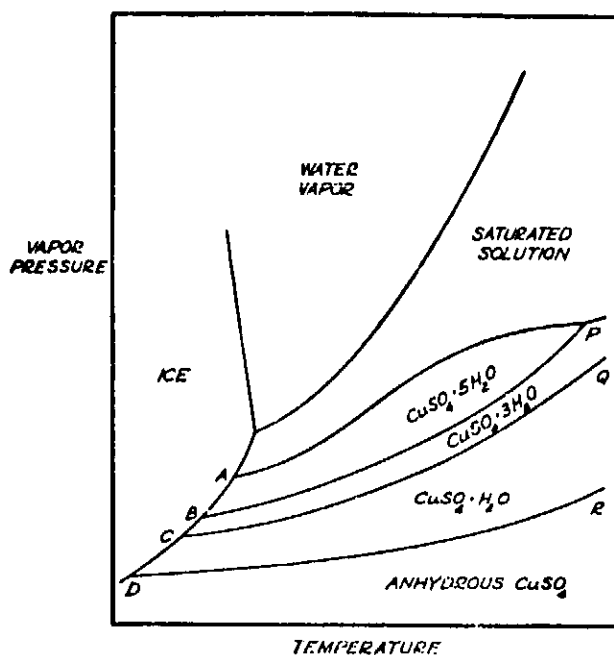
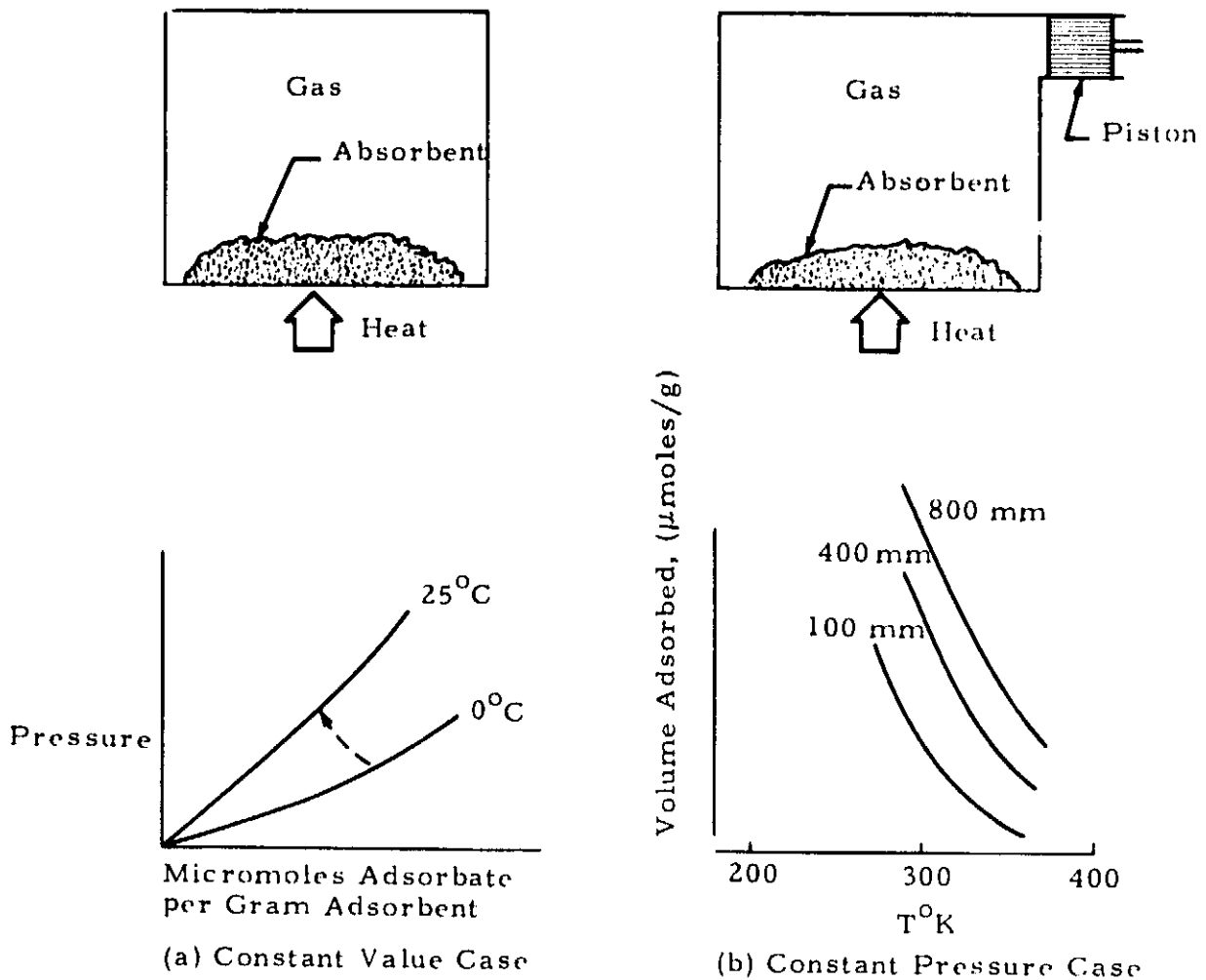


Fig. B-2 - The System  $\text{CuSO}_4$ - $\text{H}_2\text{O}$  (Ref. 12)  
(Not Drawn to Scale)

ORIGINAL PAGE IS  
OF POOR QUALITY

In considering the case of adsorption the schematics and curves shown in Fig. B-3 are helpful.

Figure B-3 shows that a closed adsorbent/adsorbate system cannot be a zero-degree system under any circumstances. Either the temperature and pressure will both rise or only the temperature will, as heat is added. Heat addition at constant temperature, however, is possible if the pressure is allowed to decrease.



ORIGINAL PAGE IS  
OF POOR QUALITY

Fig. B-3 - Illustrative Schematics for Adsorption (Ref. 13)